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FLUORIDE DETERMINATIONS IN WATER

Environmental Protection Agency
Cincinnati, Ohio

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TRAINING COURSE MANUAL

WATER QUALITY OFFICE

Water Hygiene Division

Fluoride Determinations in Water

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FLUORIDE DETERMINATIONS IN WATER

This course is designed to provide water fluoride analysis training for individuals directly involved in performing fluoride determinations on drinking waters. The fluoridation of public water supplies requires close control of dosage rates for optimum dental health benefits. Accurate analytical determinations of fluoride levels in the water are essential to control the dosage rates.

Conducted by
Water Hygiene Division
TRAINING BRANCH

Details of illustrations in
this document may be better
studied on microfiche

ENVIRONMENTAL PROTECTION AGENCY
Water Quality Office
Water Hygiene Division

Cincinnati, Ohio 45213

1971

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PUBLIC HEALTH ASPECTS OF WATER FLUORIDATION

David H. Gunderson*

I WHAT IS FLUORIDATION?

Fluoridation is the deliberate adjustment of the fluoride content of public water supplies to a level of approximately one part per million of fluoride for the purpose of reducing tooth decay. Some 10 million Americans have a naturally fluoridated water supply, and in the past twenty-five years over 4,000 communities have adjusted the fluoride content of their water.

Fluorine is the 17th most abundant element in the earth's crust. It is present in all parts of the environment-in the food, water and air, and is thus a normal constituent of all diets. Fluoridation, then, may be viewed in another way as the redistribution of a natural trace element by means of water works engineers in accordance with scientific and medical guidelines to achieve optimal levels.

II THE EXTENT OF THE DENTAL CARIES PROBLEM

A Incidence

Approximately 95% of those reaching adulthood in our country have evidence of caries. Large studies have revealed that the average American has 11 decayed teeth by age 15. Half of the population over 55 years of age have no natural teeth whatsoever. The caries lesions increase progressively in size and without treatment can lead to considerable suffering, loss of teeth and infection, which can be the source of serious systemic disease.

B Cost

In 1964, 3 billion dollars were spent in the United States for dental care, one-twelfth of the total expenditure for health care. With a concentration of 1 ppm of fluoride in the drinking water there is a 60% reduction in rate of tooth decay in children up to age 16. It has been estimated that fluoridated water systems, if available throughout the country, could in time reduce the national dental bill by one-half. The benefits expected from fluoridation then are considerable.

*Chief, Disease Studies, Water Hygiene Division, EPA

III ORIGIN OF FLUORIDATION

In 1901 research was begun to find the cause of a progressive decoloration of the teeth (fluorosis). By the early 1930's the causative agent was identified as fluorides in the water supply. It was observed, however, that these mottled teeth were resistant to cavities and there followed a number of epidemiological studies which established the protective effect against caries of drinking water containing approximately 1 ppm of fluoride.

IV SUPPORT FOR FLUORIDATION - THE NEWBURGH KINGSTON STUDY AND RELATED RESEARCH

A The Newburgh Kingston Study

During 1954-55 a study of dental health was carried out in Kingston, New York, which has non-fluoridated water, and nearby Newburgh, New York, which had been fluoridating the water a 1ppm since 1945. The children of the two communities were studied by age group. It was noted there were fewer decayed, missing or filled (DMF) teeth in all age groups of children from Newburgh compared to Kingston, the greatest benefit to children 6-9 years of age (57% fewer DMF teeth.) The proportion of children in the 6-9 year old group with all twelve primary teeth present and free of caries was over 5 times higher in the fluoride community than in the non-fluoride community.

B Aurora-Rockford Study

This involved the comparison of 18 and 19 year olds on lifetime consumption of natural optimum and low fluoride water. Young adults from Aurora (with natural optimum fluoride water) had approximately one-half the decayed teeth per person (.45 vs .96) and approximately one-half the DMF teeth per person (6.12 vs 11.90). Percentage of persons caries free was 12.5% in Aurora vs. 0.0% in Rockford.

C The Philadelphia Experience

The water supply system in Philadelphia was fluoridated in 1954 with an optimum level of 1 ppm. The effectiveness of the program was evaluated in 1964 using data collected annually by the dental examiners of the Board of Education (school children have been given dental examinations during selected grades of school since 1948 in order to determine status and needs of dental health). Evaluation of this data shows that in 1954, before fluoridation, there was approximately 1 DMF tooth for every 2 six-year olds; in 1961 the ratio was 1 DMF tooth for every 10 six-year olds, a 77% reduction in dental caries in the group who had received full benefit of fluoridation.

V MEDICAL ASPECTS OF FLUORIDATION

A Causes of Dental Caries

Tooth decay appears to be caused by civilization; when natural foods are replaced by processed foods, an increase in dental caries follows. There is now general agreement that tooth decay is of bacterial origin and that sugar must be present for bacteria to grow; adequate intake of vitamins and proteins and good oral hygiene are of great importance in preventing cavities. With the ingestion of adequate amounts of fluoride ion, the teeth are more resistant to bacterial action and fluoride promotes a resistance to dental caries beyond that afforded by adequate diet and oral hygiene. The benefits of fluoride in the water are most marked during the process of tooth development - during this period of calcification of the crown of the tooth and through the period of eruption. Resistance to decay continues throughout life, particularly for those who continue to drink fluoridated water.

B Fluorosis and Osteofluorosis

Fluorosis, or mottling of the teeth, can occur in some children who consume water containing 2 ppm fluoride during the first eight years of life; the severity of the mottling seems to bear a quantitative relationship to the fluoride level in drinking water, though regional climatic conditions influence water consumption and hence total fluoride ingested. It may occur in approximately 20%.

Osteofluorosis refers to the deposition of fluoride in the skeletal system which occurs at levels in the drinking water usually above 8 ppm; this may be seen in 10% of a population so exposed. Increased bone density is seen on X-ray and it is only at very high levels that symptoms of illness appear.

VI THE CONTROVERSY OF FLUORIDATION

A Nature and Extent of the Scientific Consensus

Fluorine, from which fluoride ions are derived, is a dangerous element, and fluoride compounds themselves are sold as commercial poisons for rodent extermination. These facts have produced considerable confusion and have at times precluded rational discussion of fluorides usefulness in the reduction of dental caries.

The biological effects of fluorides have been described in over 3,000 clinical and experimental reports in the last 30 years and includes contributions of scientists of all disciplines - biologists, chemists, dentists, physicians, and toxicologists. This research, like any research, is not free of scientific controversy; however, the overwhelming evidence indicates both the efficacy and safety of fluoridation. It has been supported by the Public Health Service, the American Dental Association, the American Medical Association, the World Health Organization and many others.

B Nature of the Opposition

There are three basic arguments raised against the introduction of fluoride compounds into the public water supply. First, antifluoridationists deny the effectiveness of fluoridation in preventing caries and stress the alleged disfiguring effects. The justification for fluoridation rests on statistics gathered in public health experiments and they challenge the validity of these data. The impressive thing is the large number of studies that have repeatedly demonstrated the value of fluoridation and it now seems that this argument is difficult to support.

Second, antifluoridationists stress health dangers involved in the use of mass fluoridation, ailments ranging from cancer to left handedness. However, mortality data from studies in Illinois, Michigan and Wisconsin demonstrate that there is no significant difference in risk of death from specific diseases such as heart disease, cancer, nephritis or diabetes. Nowhere in reports is there any evidence to support that the addition of fluoride to the drinking water increased the incidence of any

disease or indeed had any effect on health of the people except for the benefit to the childrens's teeth.

Third, antifluoridationists argue that fluoridation is a mass medication that infringes upon constitutionally protected rights of individual liberty and religious freedom. These arguments are similar to those which preceeded vaccinations against small pox, chlorination of the water and pasteurization of the milk. Although fluoridation has been challenged in the courts many times, it has been upheld in all final decisions. The court has supported the stand that fluoridation is a prudent public health policy.

ENGINEERING ASPECTS OF WATER FLUORIDATION

Thomas N. Hushower*

I WATER FLUORIDATION PRACTICE -

A Purpose

B Present Status of Fluoridation

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D Initiation of Fluoridation

II FLUORIDE COMPOUNDS -

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B Chemicals Available.

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C Handling and Storage.

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C Fluoride Dissolvers and Auxiliary Equipment.

D Fluoridating Individual Water Supplies.

E Which Fluoride Feeder Should Be Used?

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D Records

E Safety

F Maintenance

VIII LABORATORY CONTROL

IX SCHOOL FLUORIDATION

X DEFLUORIDATION

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SAFETY AND HAZARDS IN HANDLING FLUORIDES

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Despite the benefits of fluoridation against dental carries, fluorides are, under defined conditions, poisons and must, consequently, be handled cautiously.

The most critical factors which determine whether any chemical is toxic to man are the dose and the length or frequency of exposure - although other factors can and do play a significant role. There is a dose range or threshold range below which there is no toxic manifestation; and there is also a threshold range below which there is no therapeutic effect. Thus, the rationale for using fluorides at a concentration ranging between 0.8 and 1.2 ppm in the drinking water - a therapeutic effect and no toxicity under normal conditions of exposure. However, occupational exposure (such as that encountered in the application of fluorides to water supplies) may expose the workers to higher concentrations of the material and hence may increase the hazard of poisoning by fluorides.

Under working conditions, absorption of fluorides occurs either via the lungs or the gastro-intestinal tract. The inhalation and ingestion of relatively large amounts of fluoride can lead to two types of poisoning: acute and chronic.

Acute Poisoning by Fluorides. Immediate intoxication by the ingestion of fluorides is rare in industry, but various degrees of respiratory irritation may result from the inhalation of fluorides in the form of dusts. Among some of the complaints are severe biting sensations in the nose when concentrations of fluorides in the air exceeds 10 mg per cubic meter. This discomfort is usually accompanied after a few minutes by a discharge from the nose or by nosebleed. When the concentration does not exceed 2.5 mg per cubic meter, no such effects are noted. In the event of such discomfort, treatment consists of (1) removal from exposure, and (2) examination by physician in the event of nosebleed.

Acute poisoning by the oral route is usually due to confusion of sodium fluoride or other fluoride compounds with common salt or baking powder. In untreated cases, the lethal dose has been reported as 4 to 5 grams for an adult (that is, approximately 2000 times greater than the daily therapeutic dose). Since poisoning is the result of the liberation of hydrogen fluoride in the stomach, it is characterized by the typical symptoms of severe acid poisoning, that is, corrosion of the linings of the gastrointestinal tract with ulceration. The first symptoms to appear are vomiting, abdominal pains, and diarrhea. In addition, there are specific symptoms of fluoride intoxication, notably, tetany, generalized muscular weakness, difficulty in articulation, thirst, weakness of pulse, and disturbed color vision. In severe cases, there can be loss of consciousness and convulsions. Death, which is primarily due to respiratory paralysis, may occur after a few minutes but more frequently after 3 to 4 hours. Prompt initiation of therapy is essential to proper and complete recovery of the patient.

Treatment of acute poisoning by the oral route consists of:

1 Administering hot sodium chloride solution (3 teaspoonsful in a glass of water;

2 Inducing vomiting by irritating the pharynx with handle of a spoon (only if the person is conscious!);

3 Administering a glass of milk;

4 Repeating several times administration of hot sodium chloride solution; and

5 Taking individual to hospital as soon as possible.

Chronic Fluoride Intoxication (Fluorosis). Chronic poisoning by fluorides is the result of prolonged exposure to doses generally lower than those that produce acute intoxication and higher than those associated with the therapeutic effect.

The factors mainly contributing to chronic fluorosis in man are absorption and storage. Solubility of fluoride compounds ingested influences greatly the extent to which it can be absorbed. There is some experimental evidence to suggest that the accumulation of

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fluorine in the bones may exert a retarding influence upon the rate at which it is stored during chronic exposure.

Although the soft tissues contain fluorine to to the extent of 20 to 60 micrograms per 100 grams, ingested fluorine is stored chiefly in the bones and teeth. There is some controversy concerning the dose at which storage begins - some place the dose as high as 4 milligrams per day, others as low as 1.5 milligrams per day. In general the urinary fluoride excretion may be used as a rough measure of the rate at which fluorine is being stored. A remarkable parallelism between the fluorine content of the drinking water and the concentration of fluorine in the urine of a large number of human volunteers has been demonstrated, but no relation to their susceptibility to fractures of the bones could be found.

In the course of radiographic examinations of mine workers who had been exposed for several years to dusts in amounts sufficient to supply from 0.2 to 0.35 milligrams of fluorine per kilogram of body weight daily, investigators discovered a generalized osteosclerosis in many. Abnormal density and indistinct structures of the bones were most striking in the spinal column, pelvis and ribs. Over half of those who had been exposed for about 10 years presented definite evidence of changes in bone structure, varying from increased opacity of the bones to the appearance of spurs and the calcification of tendons and ligaments. In some workers the abnormalities were so pronounced as to cause stiffness of the spinal column and thorax. In few cases, consolidation of the joints of the vertebral column caused serious disability.

Other symptoms occasionally associated with fluorosis are lack of appetite, nausea, shortness of breath, constipation, localized pain in the region of the liver, and some degree of anemia. In Denmark, a slight degree of fluorosis was found in cryolite workers exposed for 2 to $2\frac{1}{2}$ years, while more definite signs were observed in those exposed nearly 5 years, and signs of moderate fluorosis appeared in those with more than 11 years of exposure. The most severe cases were those of men who had had 21 years of exposure. However, not all workers developed fluorosis, no abnormalities being detected in one man after 24 years of work.

Maximum Allowable Concentration. It is not known at present whether any rate of storage, however small, could be continued during many working years with the assurance that it would not lead to disabling skeletal abnormalities. It is therefore, impossible to state when concentration of fluorine in the urine of workers should be regarded as evidence of potentially harmful exposure to concentrations of fluorine bearing dusts that would be actually dangerous to those inhaling the air. To avoid storage completely would probably require the avoidance of more than 0.2 to 0.3 milligrams per cubic meter of air.

The following suggestions are presented to decrease exposure to fluorides:

1 Use of mask over nose and mouth while applying fluorides;

2 Working in well ventilated rooms;

3 Washing exposed surfaces of skin after applications of fluorides; and

4 Caution in handling fluorides so as to avoid dissipation of dusts.

CALCULATION OF FLUORIDE FEED RATES

John D. Pfaff*

I GENERAL:

The United States Public Health Service Drinking Water Standards stipulate that fluorides in excess of 1.7 mg/l (average air temperature 50.3 - 53.7°F.) is grounds for rejection of the water supply. The reasoning behind this statement is that fluoride content in excess of this may cause fluorosis or even death if consumed in higher quantities.

If the fluoride feed is lower than the optimum, the population will not receive the benefits of this prophylaxis.

II FLUORIDATION CHEMICALS:

The water plant operator has a wide selection of chemicals from which the fluoride may be utilized in fluoridation process. The three most popular chemicals in general use will be discussed briefly and shown in tabular form.(1)

A Sodium Fluoride: Sodium fluoride is not used in the larger plants because of its expense when compared with sodium silico-fluoride. But its solubility characteristics make it desirable in certain fluoridation installations. It is almost constantly soluable at about four per cent by weight. This property makes sodium fluoride a good chemical to use in feeders that work on the principle of saturated solutions. One does not have to weigh the chemical nor measure the water used in this type of feeder to get accurate results.

Sodium fluoride is a white, odorless, free-flowing material available either as a powder or in the form of minute crystals. The crystalline grade which contains practically no particle capable of forming dust is ideally suited for the sodium fluoride saturator tank. This material can also be used in dry feeders, but generally the powdered grades are preferred when rapid continuous dissolving is required.

Table 1

Characteristics of Fluoride Compounds

Item	Sodium silicofluoride (Na_2SiF_6)	Sodium fluoride (NaF)	Hydrofluosilicic acid (H_2SiF_6)
Form.....	Powder	Powder	Liquid
Molecular weight ...	188.05	42.00	144.08
Commercial purity, %	98.5	90-98	22-30
Fluoride ion, % (100% pure material).....	60.7	45.25	79.2
Weight (lb per cu ft).	55-72	65-90	10.5 lb/gal
Storage space, cu ft per 1,000 lb F ion.	23-30	22-34	54.73
Lb required per mg for 1.0 ppm F at indicated purity....	14.0	18.8(98%)	35.2(30%)
Solubility (g per 100 g H_2O) at 25°C (77°F).	0.762	4.05	Infinite
Gal. saturated solution required per mg water at 25°C and 1.0 ppm F	219	55.6(98%)	3.35
pH of saturated solution	3.5	7.6	1.2(1% sol)

*Chemist, Water Hygiene Division, EPA

B Sodium silicofluoride: Practically all the commercially available silicofluorides are obtained as a byproduct of the purification of phosphate rock. The known domestic phosphate reserves as of 1950 amounted to more than 13 billion tons, which contained 420 million tons of fluorine. This is enough fluorine to satisfy the needs of the water works industry for the next 27,000 years.

Hydrogen fluoride is released from the phosphate rock where it is treated with sulphuric acid in the manufacturing of fertilizer. The hydrogen fluoride is captured in limestone beds and reacts further with the impurities of the phosphate rock to form silicon tetrafluoride. This compound reacts with water to form hydrofluosilic acid. Hydrofluosilic acid is used in the manufacture of sodium silicofluoride. Sodium silicofluoride is the most popular compound used in the water fluoridation program. The primary reason for this is its low cost.

While its solubility is low, this drawback can be overcome by selecting the correct dissolving apparatus. Sodium silicofluoride is fed with a dry feeder into the solution box or dissolver which is part of all dry feeders.

Sodium silicofluoride is a white free flowing, odorless, nonhydroscopic crystalline powder. Its solubility depends on the temperature of the water. Solutions of sodium silicofluoride are corrosive. Therefore, pumps, valves, and pipes should be chosen accordingly.

C Hydrofluosilic Acid: Hydrofluosilic acid is a 20 to 25% aqueous solution of H_2SiF_6. It is not known in the anhydrous form. It is a colorless, transparent fuming corrosive liquid having a pungent odor and an irritating action on the skin. Rubber lined containers are used for shipping and storage of this acid.

While the acid is only slightly volatile, care should be observed in avoiding the vapor. Inhalation of silicon tetrafluoride can cause irritation of the respiratory tract. Equipment exposed to the fumes becomes corroded. For these reasons, storage tanks should be covered and, if placed indoors, adequate ventilation should be provided. The acid if spilled on the body should be washed off as soon as possible with water.

III RATE OF WATER PRODUCTION

All manufacturing plants have meters to determine rates of production. In the water plant this is usually measured in millions of gallons per day. In some of the smaller plants it is measured in gallons per hour.

In the fluoridation process the feeding machines are usually calibrated to feed a measured amount of the chemical per hour. Therefore, if one wants to know how many parts per million (ppm) grains per gallon, or milligrams per liter (mg/l) of fluoride he is feeding he must know how many gallons of water he is pumping per hr.

Many large plants meter production rate readings in gallons per day. To convert the unit of time to hours the production value is divided by 24 hrs per day.

Example

$$\frac{24 \times 10^6 \ \frac{\text{gal}}{\text{day}}}{\frac{24 \text{ hrs.}}{\text{day}}} = 10^6 \ \frac{\text{gal}}{\text{hr.}}$$

IV CALCULATION OF FLUORIDE FEED

A Introduction

Before we go into the calculations several notations used in this outline should be explained. When the expression ppm. or parts per million is used it can be written as

$$\frac{1 \text{ part}}{\text{million parts}} \quad \text{or} \quad \frac{1 \text{ part}}{10^6 \text{ parts}} \quad \text{the } 10^6$$

is a simple expression for the number 1,000,000. It means that 10 multiplied by its self six times will be the same as the 1,000,000 number. Now if our ppm expression is for F^- concentration it can be written as

$$\frac{1 \text{ lbs of } F^-}{10^6 \text{ lbs of } H_2O}$$

Also, if someone expresses purity as a percentage ie. Na_2SiF_6 is 60.7% pure. then this can be written as 60.7 lbs of F^- in every 100 lbs of Na_2SiF_6 or

$$\frac{60.7 \text{ lbs } F^-}{100.0 \text{ lbs } Na_2SiF_6}$$

With most of the fluoride chemicals only one term of purity, ie. x% pure, is needed. However, the hydrofluosilic acid needs two terms. This is necessary because as H_2SiF_6 is a gaseous material and in this state is only 79.2% pure. This gas is dissolved in water until an aqueous solution of appropriate concentration is achieved, usually 20 to 35%. Therefore, both terms must be used to correctly state its purity.

These two terms can be combined into one factor and used as one. This has been done in Table 2, and shows the number of pounds of F^- per one pound of certain percentages of H_2SiF_6 solution.

Table 2

H_2SiF_6 Percent.	20	22	25	26	28	30
lbs F^-/lb of % Sol.	.158	.174	.198	.206	.222	.238

B Gravimetric Feed

When a treatment plant is feeding solid chemicals, such as NaF or Na_2SiF_6, the operator is usually looking for a figure which would tell him how many pounds of chemical he should be adding per hour. The operator will know his rate of water production and hopefully what concentration, ie. ppm, of F^- he wants in the finished water. Table 1 will give the purity, expressed in F^-, of the chemical which the operator is using. With this data it is possible to calculate the rate of feed of his fluoride chemical.

In order to carry out the calculations one formula which can be used is the following:

$$Rate_1 \times Concentration_1 = Rate_2 \times Concentration_2$$

where $Rate_1$ = the rate of water production of the plant; this figure should be multiplied by an appropriate factor to convert the units to those units which fit, ie. multiply by 8.3 lbs/gal if the answer is to be expressed in lbs F^-, by 3.8 liters/gal when metric volume is wanted.

$Concentration_1$ = the concentration wanted in the final product. If a certain natural content exists it can be subtracted in this portion of the calculation.

Example: 1.2 ppm of F^- is wanted as a final conc. but 0.6 ppm F^- exists naturally. Therefore

$$\frac{1.2 \text{ lbs } F^-}{10^6 \text{ lbs } H_2O} - \frac{0.6 \text{ lbs } F^-}{10^6 \text{ lbs } H_2O} = \frac{0.6 \text{ lbs } F^-}{10^6 \text{ lbs } H_2O}$$

$Rate_2$ = This is the rate at which the fluoride chemical must be fed inorder to produce the desired concentration of F^-.

$Concentration_2$ = This is really an expression for the purity of the fluoride chemical. This number can be obtained from Table 1. If the chemicals were 100% pure this correction would not be necessary however since most of the fluoride chemicals contain only a fraction of fluoride it is necessary.

Some examples of the use of this formula are shown next.

Example 1:

How many lbs of F^- should be fed in a 1 MGD plant that uses Na_2SiF_6 and needs a 1.2 ppm conc. of F^- in the final product.

Example 2:

If a plant produces 200 gal per minute and wishes to feed 28% H_2SiF_6 until a 1.2 ppm fluoride content is carried in its final effluent, at what rate should this H_2SiF_6 be fed expressed in pounds per hour.

C Solution Feeds:

In many small plants the fluoride is made up into solutions and fed as a liquid. Machinery for feeding such liquids will in all probability be calibrated in milliliters per minute.

Fluoride in a quantity of feed solution will be diluted upon its addition to water produced by the plant. The rate of feed is equal to the rate of H_2O production multiplied by the desired concentration of fluoride in the H_2O all of which is divided by the concentration of fluoride in the feed solution.

A saturator for example under proper conditions will feed a constant 4% of NaF to the treated water. This 4% solution is approximately 18,000 ppm F. Using this figure of 18,000 ppm F^- the rate of feed can easily be calculated using the same formula as we have been using.

Example 3:

A 20,000 gpm plant using a saturator wishes to have 1.2 ppm F^- into finished water at what rate in milliliters per/min should they feed.

D Example Solutions:

Example #1

$$R_1 \times Conc_1 = R_2 \times Conc_2$$

$$\frac{1 \times 10^6 \text{ gal}}{\text{day}} \times \frac{8.3 \text{ lbs } H_2O}{\text{gal}} \times \frac{1 \text{ lbs } F^-}{10^6 \text{ lbs } H_2O} = x$$

$$\times \frac{60.7 \text{ lbs } F^-}{100 \text{ lbs } Na_2SiF_6}$$

$$\frac{\dfrac{8.3 \text{ lbs } F^-}{\text{day}}}{\dfrac{.607 \text{ lbs } F^-}{\text{lbs } Na_2SiF_6}} = x = 13.67 \frac{\text{lbs } Na_2SiF_6}{\text{day}}$$

Example #2

$$\frac{200 \text{ gal}}{\text{min}} \times \frac{8.3 \text{ lbs } H_2O}{\text{gal}} \times \frac{1.2 \text{ lbs } F^-}{10^6 \text{ lbs } H_2O} = x$$

$$\times \frac{.222 \text{ lbs } F^-}{\text{lbs of 28\% sol.}}$$

$$\frac{\dfrac{1992 \text{ lbs } F^-}{10^6 \text{ min}}}{\dfrac{.222 \text{ lbs } F^-}{\text{lbs of 28\% sol}}} = x = \frac{8973 \text{ lbs of 28\% sol}}{10^6 \text{ min}}$$

$$x = \frac{.009 \text{ lbs of 28\% sol}}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}}$$

$$x = \frac{0.54 \text{ lbs of 28\% sol}}{\text{hr}}$$

Example #3

$$Rate_1 \times Conc_1 = Rate_2 \times Conc_2$$

$$20,000 \frac{\text{gal}}{\text{min}} \times .2 \text{ ppm} = x \times 18,000 \text{ ppm}$$

$$\frac{\dfrac{24,000 \text{ gal} \times \text{ppm}}{\text{min}}}{18,000 \text{ ppm}} = x = 1.33 \frac{\text{gal}}{\text{min}}$$

$$x = 1.33 \frac{\text{gal}}{\text{min}} \times \frac{3.8 \text{ l}}{\text{gal}} \times \frac{1000 \text{ ml}}{\text{l}}$$

$$x = 5054 \frac{\text{ml}}{\text{min}}$$

COLORIMETRIC ANALYSIS

I BASIC PRINCIPLES OF COLOR MEASUREMENT

Colorimetric analysis is based upon the relationship of the color intensity of a solution to the concentration of a colored substance in the solution. By a suitable systen of measurement, this relationship can be established and used as a quantitative analytical method. This system utilizes three basic components: a source of radiant energy, a sample positioning device, and a receptor or detector of radiant energy values (Figure 1). Regardless of their refinement or complexity, all colorimetric methods depend upon the manipulation of these three essential parts.

A Source of Radiant Energy

The first requirement for colorimetric analysis is a source of radiant energy. In the visible region of the spectrum, where color is produced, the radiant energy is visible light. For the simpler techniques, the source of light may be sunlight from a window, or artificial room illumination. More refined instrumental methods require carefully controlled sources. These are usually tungsten filament bulbs, operated at constant voltage.

To insure satisfactory measurement of color values, the source of light must be of constant intensity and should contain all the wave lengths between 400 and 700 mμ. In other words, it should be white light, rather than colored light. For special purposes, filters and other devices may be used to produce pure colored light from the basic white.

B Sample

The colored solution to be measured is placed in a sample cell or cuvette. The cell is positioned so that light from the source must pass through to the dectector. The cell must have a fixed light path; that is, the light must pass through a definite thickness of sample. Solutions to be compared are placed in the same cell, or in matched cells having the same light path. For visual comparison long light paths (30 cm) are needed, while 1-5 cm. are sufficient for most instrumental methods. The reasons for careful control of light path will be detailed in the section on Quantitative Factors.

C Detector

The detector measures the relative intensity of the light after it has passed through the sample. A satisfactory detector must be capable of measuring all wavelengths of visible light, as well as detecting small changes in intensity. In some colorimetric systems the human eye is the detector, while in others a light-sensitive photocell is used.

D Light Absorption

Light from the sun or from an electric lamp is a combination of many different colors, all blending to give white. When white light passes through a colored solution, some of the colors in the white are absorbed by the solution and some are passed through or transmitted. The wavelengths of light absorbed or transmitted will depend upon the color of the light from the source and the color of the solution. Figure 2 shows the case of white light striking a green solution. Note that most of the red light is absorbed but the green and yellow is transmitted. If the solution is blue the orange and yellow will be absorbed but the blue will be transmitted.

If the source light is colored, it will be partially absorbed by certain wavelengths but practically unchanged by others. In Figure 3 green light from Source G and yellow light from Source Y are striking the red solution. The green is almost completely absorbed while the yellow is only partially absorbed.

Thus the red solution has greater effect on green light than on yellow, and changes in the strength of the red solution will produce large changes in the amount of green light absorbed but only small changes in the yellow.

FIG. 1

COLOR MEASUREMENTS SYSTEM

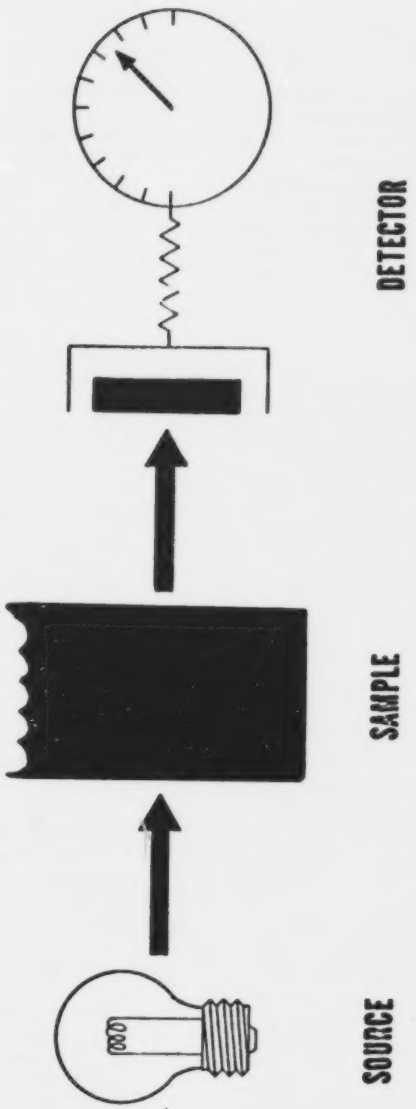


FIG. 2

COLOR AND LIGHT ABSORPTION

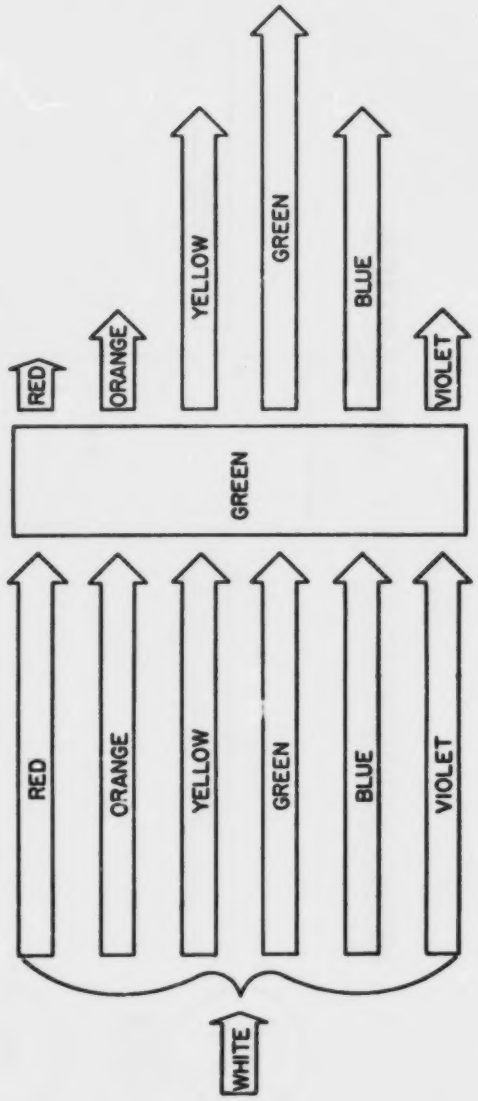
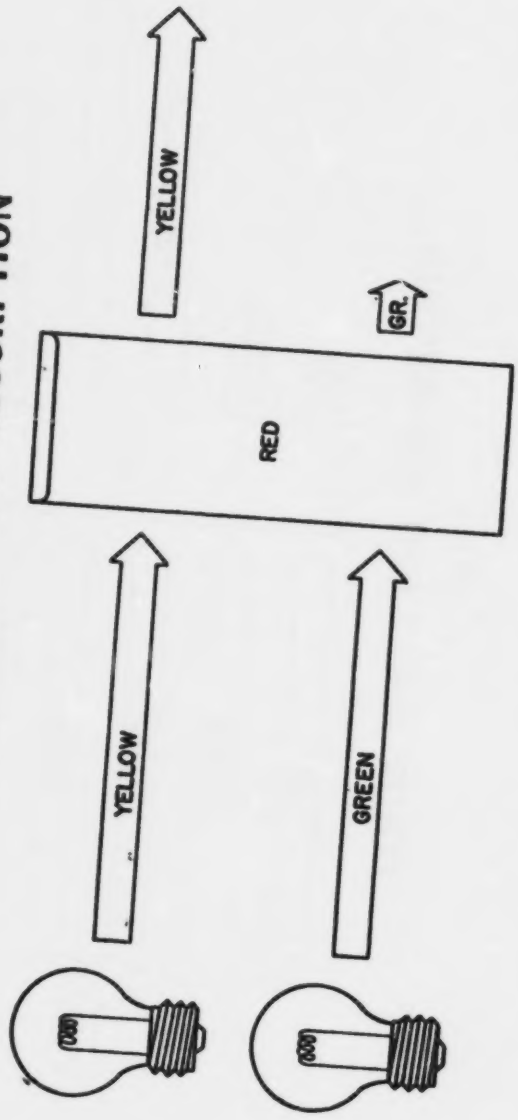


FIG. 3

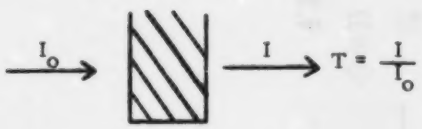
MONOCHROMATIC LIGHT ABSORPTION



E Quantitative Factors

In order to relate the amount of light absorbed by a solution to the concentration of a colored constituent, certain mathematical terms must be defined.

Transmittance (T) - the ratio of the light which passes through the cell to the light which strikes the cell initially.



T is always less than one but is usually expressed as a percent of the initial light.

Absorbance (A) - the amount of light absorbed by the sample.

$$A = 1 - T$$

Optical Density (O. D.) - a logarithmic term expressing the absorbancy of the sample.

$$O.D. = \log_{10} \frac{1}{T} = \log_{10} \frac{1}{\frac{I}{I_o}} = \log_{10} \frac{I_o}{I}$$

Since it is the logarithm of a positive number, OD must be greater than zero and is usually measured between 0 and 2.0.

II LAWS OF COLOR ABSORPTION

Using the concept of absorbance, definite laws have been formulated to express the relationship of the amount of absorption to the quantity of the absorber.

Bouguer Law of Absorbancy and Thickness: Each layer of equal thickness absorbs an equal fraction of the light which traverses it.

In an homogeneous solution each layer contains the same number of molecules of the absorber and would therefore absorb the same fraction of light. If the light travels through five thicknesses of sample, five times as many molecules would be encountered and thus the absorption would be proportionally greater. In Figure 4 the effect of a cell path of 1 cm is compared with one of 5 cm. Since the absorptive capacity varies logarithmically with thickness, the percent absorbed is only 3.4 times as great, but the Optical Density is 5 times as great.

Beer's Law of Absorbancy and Concentration: The amount of light absorbed by the sample is directly proportional to the concentration.

Thus if Sample A were 1.5 times as concentrated as Sample B there would be 1.5 times as many molecules present to absorb the light. The absorption varies logarithmically with concentration, so the Optical Density is a direct measure of the concentration. In Figure 5 the higher concentration absorbs more light and the optical density is 1.5 times greater. The calibration curve shows the linear relationship between concentration and Optical Density.

Most colored systems conform to Beer's Law. In some cases the higher concentrations cause scattering of the light and a simple logarithmic relationship does not hold. In other cases a colloidal solution is formed which does not follow the absorbance principle.

III COLOR MEASUREMENT SYSTEMS

A Nessler Tubes

Visual comparison methods, involving Nessler tubes, are widely used in colorimetric analysis. These tubes are available in either tall form (30 cm light path) or in low form (15 cm light path). They are graduated at 50 ml or 100 ml volume.

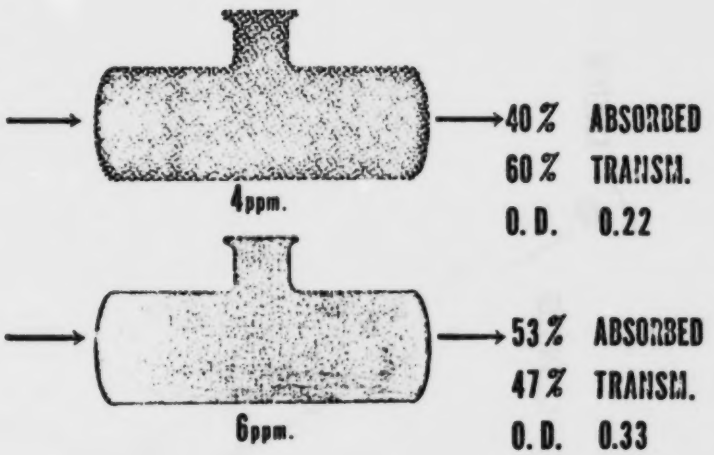
It is important that the tubes in each set are matched so that differences in length of light path are negligible. In addition, the set should be of the same glass composition, as glass tints may effect the color differences. When working with Nessler tubes, day light or room light is the source, the long tube is the sample container, and the human eye is the detector. (Figure 6).

FIG. 4

BOUGUER—LAMBERT LAW OF ABSORPTANCE

FIG. 5

BEER'S LAW OF ABSORPTANCE



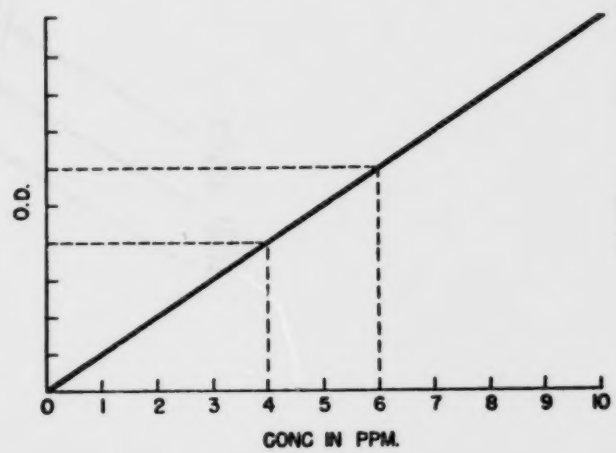
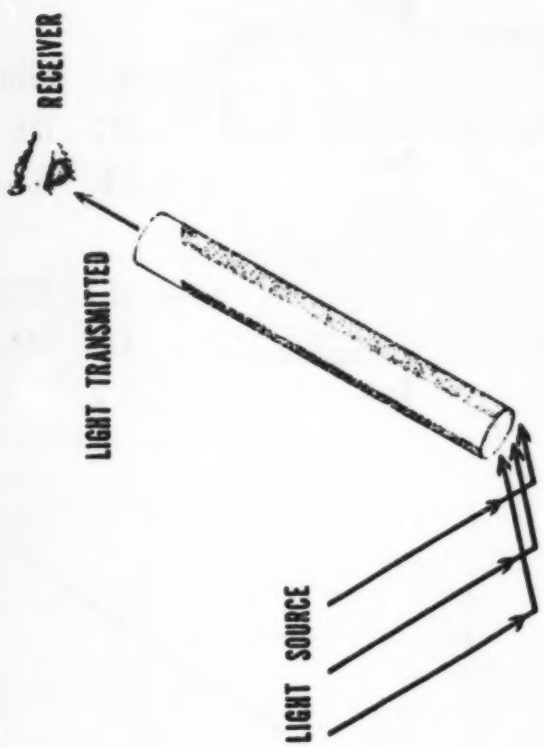


FIG. 6
BASIC PRINCIPLE - OPTICAL MEASUREMENT



The tubes are held in such a way that light from the window or lamp passes longitudinally through the tubes. The sample and standards are compared and the sample is "matched" with one of the standards. The unknown concentration is then equivalent to the concentration of the matching standard.

Nessler tubes have both advantages and disadvantages. They are very simple, are inexpensive, and because of the long light path, offer good sensitivity. In most cases the color development reactions can be carried out directly in the tube.

The disadvantages stem from the necessity for visual comparison of the tubes. First, since laboratory workers vary greatly in their ability to distinguish small differences in color intensity, the determination may vary in accuracy between several workers. As shown above, the quality of the light from the source will effect the absorption by the sample. Therefore changes in room illumination may significantly change the interpretation of the color comparisons.

Further, the human eye is not equally responsive to all wavelengths of light in the visible range. Figure 7 shows a graph of the response of the eye to various wavelengths. Note that sensitivity drops off rapidly in the upper (deep red) and lower (purple) ends of the scale. Thus the ability to distinguish small changes in color is restricted to blue-green-yellow solutions. Color comparisons in purple and deep red solutions are not nearly as good.

One additional limitation should be mentioned. The eye has poor "memory sense." Color comparisons must be made simultaneously in order to judge the color match. This requires the use of a series of color standards each time a determination is made.

B Color Comparators

The principles of visual comparison by matching standards, as used in the Nessler tube technique, has produced a number of allied methods. Modification of the tubes to reduce the size and bulk, the use of permanent standards, standardization of the source, and control of the positioning of the components, have all been used to make comparison easier and faster.

1 Liquid standards

Preparation of a series of standards, as described in III A, is laborious and time consuming. In some cases the color complex is sufficiently stable to permit reuse of the standards over a long period but in others the color reaction is so transient that readings must be made immediately.

To eliminate the necessity for preparing fresh standards each time the determination is made, permanent standards have been developed for many tests. Such standards are made either from colored glasses or plastics or from colored solutions sealed in tubes. When the actual colored solutions in the test are unstable, the standards are made from other more stable solutions having the same color characteristics.

2 Color discs

Glass color discs have been developed, which are made to match the color of the test solutions as nearly as possible. The Hellige Aqua Testor, shown in Figure 9 is an example of this type of instrument. The color discs are mounted in a wheel which can be revolved to bring the standards into position alongside the test solution. Color discs are available for many different determinations. Illumination is provided by a light bulb in the base of the instrument.

C Filter Photometers and Spectrophotometers

Because of the deficiencies of room light as a source and the human eye as a detector, instruments have been developed which incorporate a constant light source

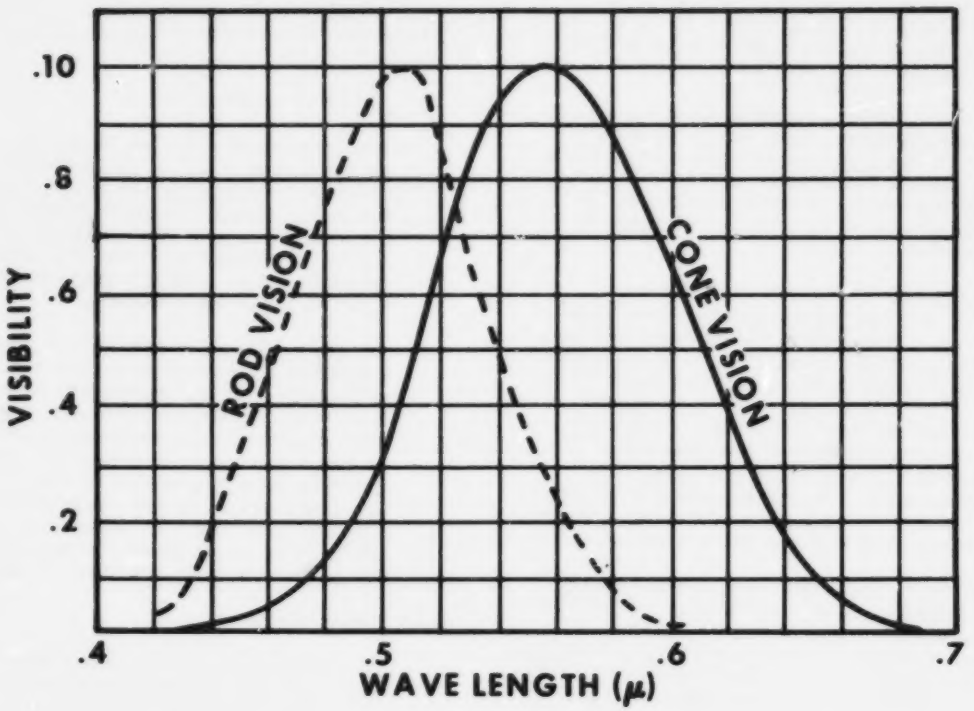


FIG. 7
VISIBILITY CURVES

TABLE OF COLOR AND WAVE LENGTHS

0.723 μ to 0.647 μ ▪ Red	0.575 μ to 0.492 μ ▪ Green
0.647 μ to 0.585 μ ▪ Orange	0.492 μ to 0.455 μ ▪ Blue
0.585 μ to 0.575 μ ▪ Yellow	0.455 μ to 0.424 μ ▪ Indigo

0.424 μ to 0.397 μ ▪ Violet

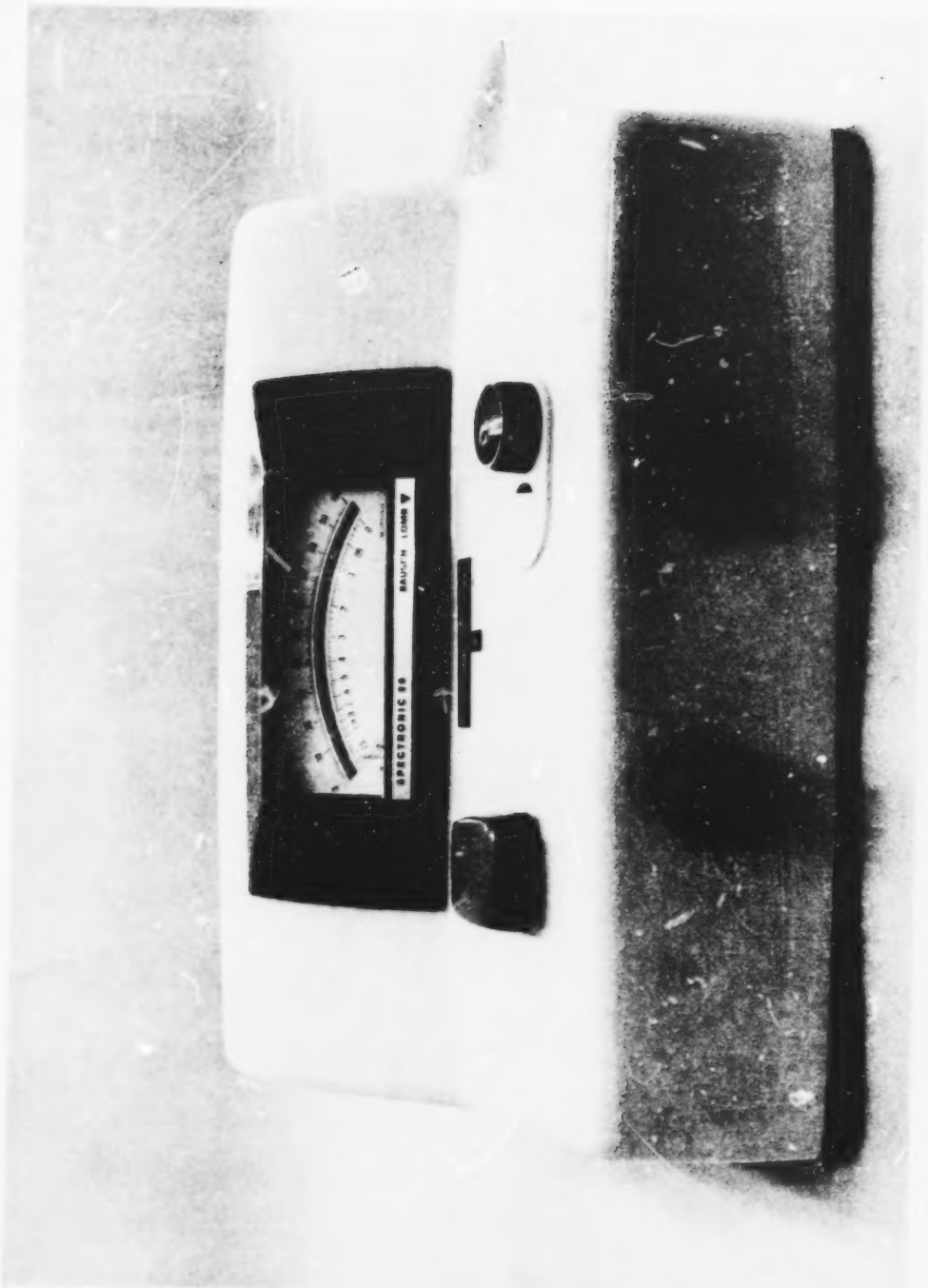
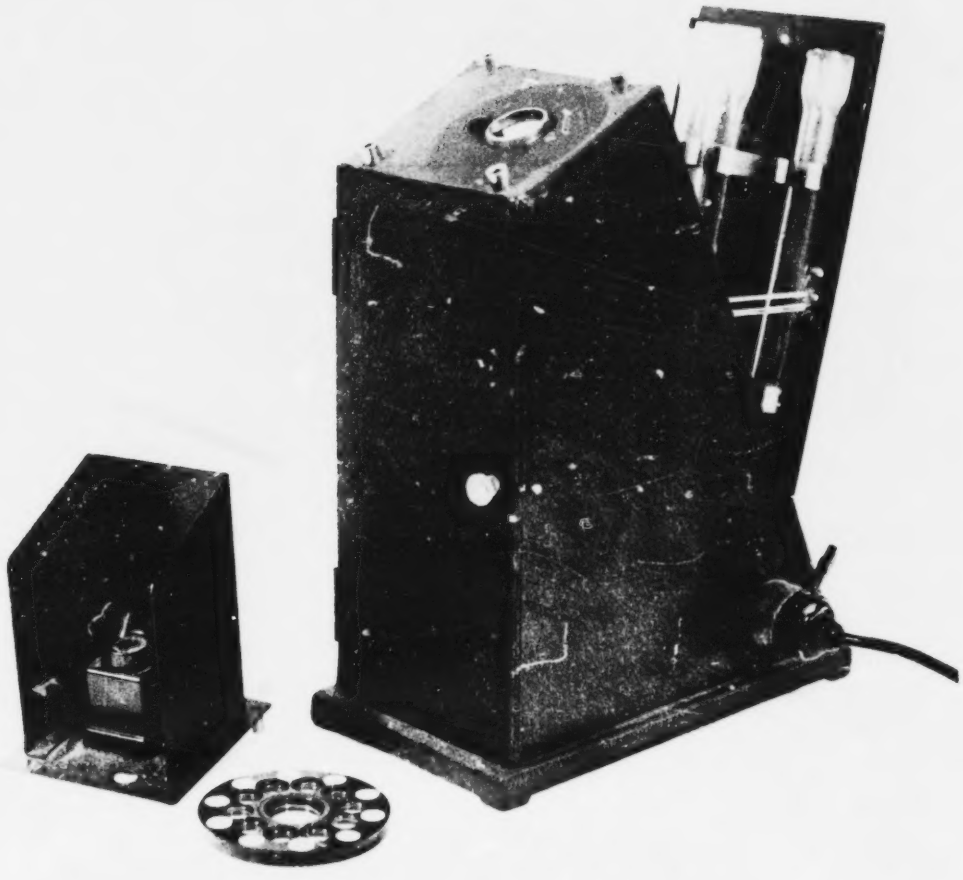


Figure 8

FIG. 9
HELLIGE AQUA TESTOR



(tungsten lamp) and a photoelectric detector. These instruments called photometers, have several definite advantages over visual methods. The built-in lamp stabilizes the intensity and color of the source and the phototube provides an impersonal evaluation of the light intensity transmitted by the solution. When used with an indicating meter the phototube provides numerical values for light intensity which can be used for the construction of standard curves. Such curves eliminate the need for preparing fresh standards.

When photocell detectors are used the sensitivity provided by monochromatic light is an advantage. For this reason photometers are equipped with some means of modifying the light from the source to a narrow band of pure color. This may be accomplished by a filter placed in the light beam from the source. In Figure 10 the light from the source passes through a green filter, allowing only green light to reach the sample.

When a photometer is used for several different colorimetric determinations, a complete set of filters may be required. Methods designed for photometric measurement generally specify the best wave length to use.

Spectrophotometers are instruments which have a mechanical means of providing any desired wave length. In most spectrophotometers the light from the source is passed through prism or grating where the light is broken up into the spectrum (Figure 11). By controlling the prism and slit any desired color may be passed to the sample. In addition to the versatility provided most spectrophotometers offer better color selectivity (narrower slit width) and higher sensitivity to changes in light intensities. (Figure 8)

IV DETERMINING THE CONCENTRATION OF UNKNOWNS USING PHOTOMETRIC INSTRUMENTS

A Standard Curves

When using a photometric instrument, the instrument readings can give quantitative factors for measuring the concentration of test substances.

In use a series of standards are prepared as described under Nessler tubes (III-A). Beginning with the blank, containing the color formation reagents but none of the test substance, the percent transmittance or Optical Density of each standard is measured using the optimum wavelength. A curve is plotted, with concentration on the lower line and T or O. D. on the left margin. Typical curves are shown in Figure 12.

When an unknown sample is to be analyzed the reagents are added and the transmittance or Optical Density measured in the same way as with the standards. From the values the concentration of the unknown can be determined by reference to the standard curve.

B Use of Curves

In Figure 12 the three common methods of plotting calibration curves are illustrated. The upper curve, percent transmission vs. conc. gives a logarithmic curve. Such a curve is difficult to draw precisely and has low sensitivity in the high concentrations. The center curve employs the same T values but utilizes semi-log paper. The result line is straight but has a negative slope (slants downward from 0 concentration). Since the T values are logarithmic, it is difficult to calculate a calibration factor.

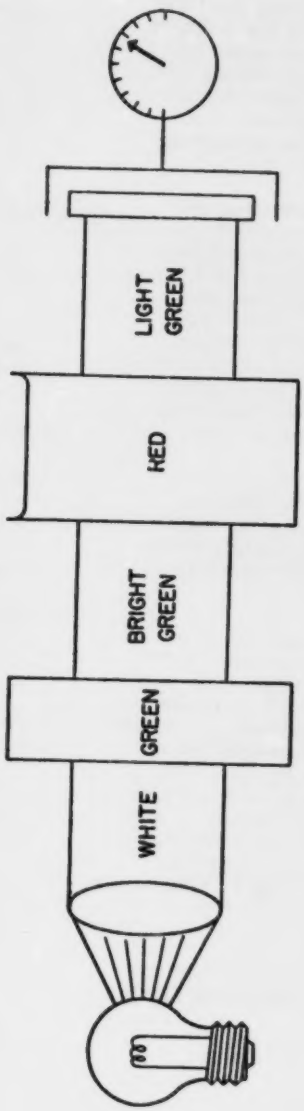
The lower curve plots Optical Density values instead of transmittance. Linear graph paper is used and the line has positive slope. Since it is straight, the line can be drawn precisely. A simple mathematical relationship exists between the O. D. values and concentration.

$$\text{Conc.} = \text{O. D.} \times k$$

Where "k" is a simple number derived from the curve.

FIG. 10

FILTER PHOTOMETER



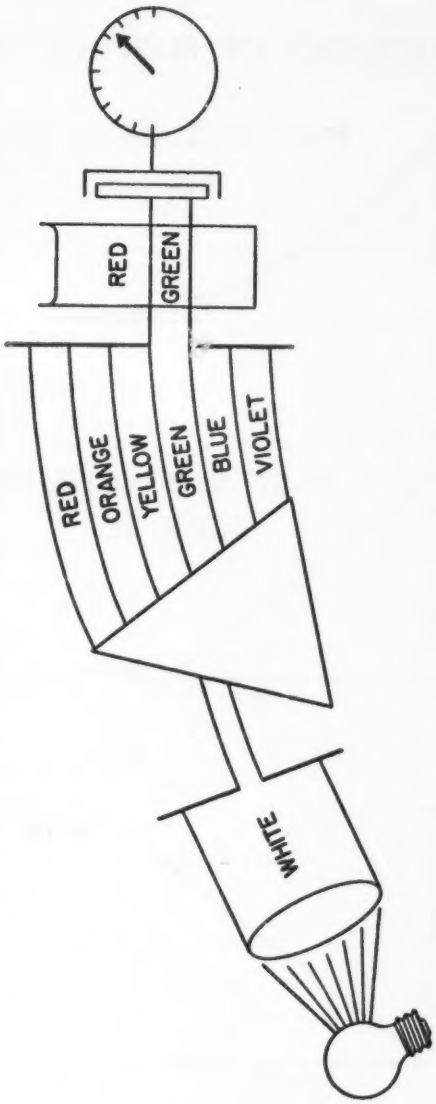
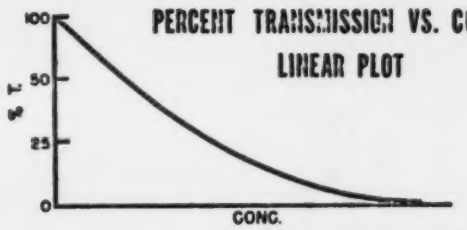


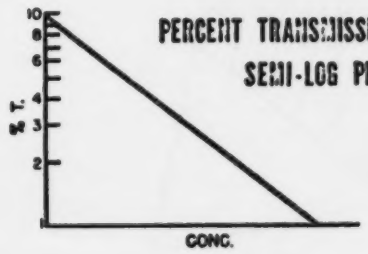
FIG. II
SPECTROPHOTOMETER

FIG. 12

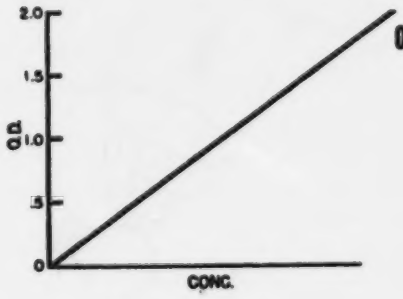
METHODS OF PLOTTING RESULTS



PERCENT TRANSMISSION VS. CONC.
LINEAR PLOT



PERCENT TRANSMISSION VS. CONC.
SEMI-LOG PLOT



OPTICAL DENSITY VS. CONC.
LINEAR PLOT

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CHEMISTRY OF FLUORIDE ANALYSIS

I INTRODUCTION

The analysis of fluoride in water concerns the determination of the quantity of fluoride ion present in solution, irrespective of the source of that ion. It may come from fluoride compounds occuring naturally in the water, or from fluoride or silicofluoride compounds added to the water. There is no method for distinguishing one fluoride ion from another.

II ANALYTICAL METHODS

Because of the quantities of fluoride normally found in drinking water are so small, the analytical method must be adapted to the measurement of these quantities.

A Gravimetric methods involve the precipitation of fluoride as part of a heavy complex, so that sufficient material can be obtained for accurate weighing.

B Volumetric methods usually entail concentration of the sample so that the volume of titrant is large enough to be measured accurately. In addition, the color change of the indicator at the endpoint is extremely difficult to detect.

C Other methods are available, such as polarographic and potentiometric, but these involve expensive and elaborate equipment, and furthermore are not well adapted to small quantities of fluoride.

D Until recently, the best analytical methods for determining fluoride in water were the colorimetric methods, and two of those in Standard Methods belong to this category. The colorimetric methods are sensitive to minute quantities of fluoride and are easily performed with the simplest type of glassware and instruments.

E The development of an electrode which is almost completely specific for fluoride ions has revolutionized the field of fluoride analysis. The electrode method is extremely sensitive and requires, in addition to the fluoride electrode itself, only an ordinary pH reference electrode and an expanded-scale pH meter (or digital meter) for the analysis of waters containing any likely concentration of fluoride.

III THE COLORIMETRIC REACTION

The basis for two of the fluoride methods now listed in Standard Methods is the zirconium-dye reaction. In this reaction, a red lake is produced by the combination of dye and zirconium. Any fluoride present in the water sample removes zirconium from the reaction, thus decreasing the intensity of color present.

A The visual Scott-Sanchis method uses alizarin as the dye. In water samples which are high in fluoride, the only color apparent is the yellow color of the unreacted dye. Conversely, in low fluoride samples, the color approaches the deep red of the zirconium-alizarin lake. Intermediate fluoride concentrations give colors which are intermediate between the two. (Figure 1) The colors are all relatively pale and are adaptable for viewing through long Nessler tubes. The reaction is not an immediate one, but progresses with time. After one hour the reaction rate is extremely slow, and for this reason the time interval between adding reagent and making the measurement has been selected as 60 minutes. The reaction rate is affected by a number of factors, among them the acidity and temperature of the reaction mixture.

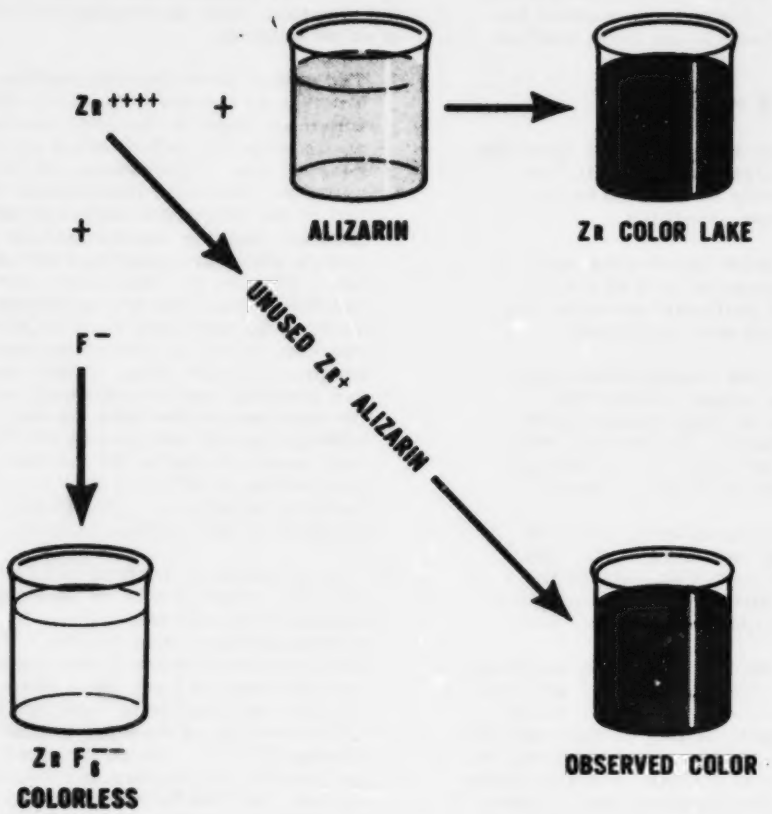
B The photometric method used SPADNS as the dye. (SPADNS is an abbreviation of sodium 2-(p-sulfophenylazo)-1, 8-dihydroxy-3, 6-napthalene disulfonate). The color of the reaction mixture (water sample plus reagent) varies from very deep red in the absence of fluoride to light red when the concentration of fluoride is high. The change in color caused by small changes in fluoride concentration is indiscernible by eye, but can be readily detected by a photometric instrument. The better the instrument, the better the sensitivity to small increments of fluoride. The acid concentration of the reagent is much higher than that of the visual method, making the reaction virtually instantaneous.

IV OTHER COLORIMETRIC METHODS

Besides these Standard Methods, many other colorimetric fluoride methods are available.

FIG. 1

THE ALIZARIN-ZIRCONIUM REACTION



Many of these are designed to eliminate the one-hour waiting period, or at least to shorten it, since this is the principal drawback of the zirconium-alizarin method.

A The Rubin method is a visual technique which utilizes permanent artificial standards. The color reaction is still that of the zirconium-alizarin method and as such must be carefully timed.

B The ECR (Eriochrome Cyanine R) photometric method is similar to the SPADNS method in that it uses a high acid concentration causing the reaction to be almost instantaneous. While the advantages of the reagent, such as speed, sensitivity and tolerance to many interferences make it quite useful, it has two distinct disadvantages. These are its intolerance for sulfate and the requirement for spectrophotometric measurement. The sulfate can be analyzed for separately, and appropriate compensation made, but the extra analytical step greatly increases the possibility of error. The necessity for using a spectrophotometer limits use of the method to laboratories which are equipped with this instrument.

C The Alizarine Complexone methods use a different color system. Since the color change is from blue to red with increasing amounts of fluoride, the use of a red filter will produce a calibration curve with positive slope. The reaction is not immediate, but slow enough so that fluoride can be measured after a 15-minute waiting period. Other disadvantages are that the reagent is not too stable and tolerance to aluminum is particularly poor.

V PHOTOMETRIC VS VISUAL METHODS

In general, the photometric methods are to be preferred over visual techniques, since their advantages far outweigh their disadvantages.

A The ability to obtain more accurate analyses, and the virtual elimination of the human element are qualities inherent in an instrumental technique. Furthermore, the reagents available for photometric methods are more sensitive and more stable. The infrequent preparation of a standard curve is a more preferable operation than the prepartion of visual standards for each set of samples. With a small amount of manipulation, a photometer can be used to compensate for color and turbidity in the water sample, although distillation is usually preferred in such cases.

B On the debit side of the ledger, a photometer is admittedly more expensive than is a set of Nessler tubes, although the expense can often be justified by the multiple analyses for which the photometer can be used. Another disadvantage of a photometric method, sometimes applicable to visual methods as well, is that glassware must be scrupulously clean in order to avoid changes in the light transmittance of the sample cell itself.

VI SOURCES OF ERROR IN COLORIMETRIC ANALYSIS

The analysis of water is a comparatively delicate operation - the quantities involved are minute, and the greatest possible accuracy is desirable. For these reasons, no possible source of error can be overlooked.

A The reagent, which contains not only the components which form the color lake, but also the acid for achieving the desired pH, must be accurately measured. This implies the correct pipetting technique.

B Glassware, whether Nessler tubes or photometer cells, must be clean and perfectly matched.

C When treated water samples are being analyzed, the presence of chlorine must always be suspected, and when necessary, the chlorine eliminated with arsenite. The use of thiosulfate for this purpose should be discouraged, since an excess can produce turbidity in the sample.

D Although color and turbidity can be compensated for in some cases, it is always best to distill such samples.

E Analytical results obtained with any of the colorimetric reagents are limited to a very narrow range of fluoride values, and samples which approach or exceed the limit of the range must be appropriately diluted. The dilution must be made before addition of reagent, since subsequent dilution will affect the concentration of dye, zirconium and acid.

F While exact timing is not important in the visual method, it is imperative that

both standards and samples be treated with reagent as nearly simultaneously as possible so that the color development will progress to the same degree in each. In any method, temperature of samples must match standards or the standard curve.

G Perhaps the most important source of error is the presence of interfering ions in the water sample. It is readily conceded that none of the colorimetric methods is entirely specific for fluoride, and to varying degrees many of the other ions found in water affect the fluoride analysis. The reagents are designed to provide as much tolerance as possible for these interfering ions, but when the limits of tolerance are exceeded, or when any doubt exists as to the presence or quantity of such interferences, the water sample must be distilled before an accurate fluoride analysis can be made.

VII THE ELECTRODE METHOD

The basis for this method is in the fluoride electrode itself. Most electrodes contain a fluoride solution; at the tip of the electrode is a crystal doped with fluoride ions. The crystal acts as an ion-exchange membrane, so that when the fluoride concentration outside of the electrode is higher than that inside, ions move toward the inside setting up a voltage potential proportional to the difference in fluoride concentration. Conversely, when the fluoride concentration on the outside is lower than that on the inside, a proportional potential of opposite sign is set up. In most fluoride electrodes, the internal solution is about 10^{-3} molar in fluoride, so concentrations below 19 ppm result in positive voltage readings. Some electrodes contain no internal solution, but the principle of operation is similar. However, in the solid electrodes the potential developed by a particular fluoride solution is independent of a filling solution but rather depends entirely on the characteristics of the particular crystal used in the electrode manufacture.

A The electrode measures ion activity only, so that fluoride present in un-ionized form will not be detected. At low pH's, when un-ionized HF is present, and in the presence of complexing agents like aluminum, for example, low readings will result. The only known interference is hydroxide ion, but for practical purposes, aluminum and other complexing agents must also be considered as interferences since they affect the formation of fluoride ions.

B A system has been developed whereby the electrode can be used to detect fluoride concentration instead of fluoride ion activity. The system utilizes a buffer mixture which, when added to the sample, controls the pH, ties up complexing agents and provides a high ionic strength background so that ion activity remains proportional to concentration. When this buffering system is used, most water samples can be read directly, without dilution regardless of concentration, and without regard to color, turbidity, etc. The only likely interference is aluminum in relatively high concentration, and even this can be overcome by making a small adjustment to the buffer composition.

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FLUORIDE ANALYTICAL PROCEDURES – SCOTT-SANCHIS

1 SCOTT-SANCHIS COLORIMETRIC METHOD

A Reagents

1 Acid-Zirconium Reagent

a Dissolve 0.3 g zirconium chloride ($ZrO\ Cl_2 \cdot 8H_2O$) or 0.25 g $ZrO(NO_3)_2 \cdot 2H_2O$ in 50 ml. dist. water in a 1 liter flask.

b Dissolve 0.07 g sodium alizarin monosulfonate in 50 ml. dist. water.

c Add the alizarin solution to the zirconium solution in the flask, while swirling. Allow the resulting solution to stand for a few minutes.

d Dilute 101 ml. conc. HCl to approx. 400 ml with dist. water.

e Carefully add 33.3 ml. conc. H_2SO_4 to approx. 400 ml. dist. water. After cooling, mix the two acids.

f To the clear zirconium-alizarin solution in the 1 liter flask, add the mixed acids and dilute to the 1 liter mark and mix. Allow to stand one hour before use. When stored away from sunlight, the reagent is stable for at least six months.

2 Fluoride Stock Solution

a Dissolve 0.2210 g NaF in 1 liter of dist. water (1 ml = 0.1 mg F).

3 Standard Fluoride Solution

a Dilute 100 ml. of the above stock solution to 1 liter (1 ml. = 0.01 mg F).

4 Sodium Arsenite Solution

Dissolve 5.0 g $NaAsO_2$ in 1 liter of dist. water.

B Procedure

1 Prepare a series of fluoride standards by pipetting the indicated amounts of the standard fluoride solution into 100 ml., Nessler tubes and diluting to mark.

ml Standard Soln.	mg. F	ppm F
0	0.00	0.0
2	0.02	0.2
4	0.04	0.4
6	0.06	0.6
8	0.08	0.8
10	0.10	1.0
12	0.12	1.2

2 Take 100 ml. of the sample, or an aliquot diluted to 100 ml, in a 100 ml. Nessler tube and dechlorinate by adding 1 drop (0.05 ml) of the arsenite solution for each mg/l chlorine present in the sample.

3 Adjust the standards and sample to the same temperature, within $\pm 2^{o}C$.

4 Add 5 ml of the mixed reagent (above) to each of the standards and sample. Mix well and allow to stand at least 60 minutes.

5 Compare the sample with the standards and determine the amount of fluoride present in the sample aliquot.

6 Report fluoride concentration in ppm.

FLUORIDE ANALYTICAL PROCEDURES – SPADNS

I SPADNS PHOTOMETRIC METHOD

A Reagents

1 Dissolve 0.958 g. SPADNS in distilled water and dilute to approximately 300 ml in a 1-liter volumetric flask.

2 Dissolve 0.133 g zirconyl chloride in about 200 ml distilled water and add to the flask.

3 Add 350 ml concentrated HCl and dilute to 1 liter.

4 Fluoride stock solution: 0.2210 g NaF dissolved in 1 liter distilled water (1 ml = 0.1 mg F).

5 Standard fluoride solution: dilute above stock solution 1:10 with distilled water (1 ml = 0.01 mg F) (or dilute 1:100 to make 1.0 ppm F standard).

6 Sodium arsenite solution: 5.0 g $NaAs O_2$ dissolved in 1 liter distilled water.

B Procedure

1 Prepare two separate standards as follows:

a 0 ppm standard - carefully measure (with a volumetric pipet) 50 ml of distilled water.

b 1.0 ppm standard - carefully measure (with a volumetric pipet) 50 ml of 1.0 ppm F standard solution.

2 Carefully measure 50-ml portions of each unknown sample.

3 Add 10 ml of reagent to each standard and sample.

4 With the distilled-water standard (0 ppm F) in the cuvette, adjust the photometer slit so that a reading of .300 or .500 on the absorbance scale is obtained. Use a wavelength of 570.

5 Replace the 0 ppm standard with the other standard and samples in succession, noting the absorbance reading in each case.

6 Calculate the fluoride content of the unknown samples by the formula:

$$X = \frac{A_o - A_x}{A_0 - A_1}$$

where X is the fluoride content of the sample in ppm,

where A_o is the absorbance reading of the 0 ppm standard,

where A_x is the absorbance reading of the unknown sample, and

where A_1 is the absorbance reading of the 1.0 ppm standard.

If preferred, a curve may be drawn by plotting the absorbance readings of the two standards and connecting with a straight line. The line may be extended to 1.4 ppm, but no further.

FLUORIDE ANALYTICAL PROCEDURES - ELECTRODE

I ELECTRODE METHOD

A Reagents

1 TISAB

a Place approximately 500 ml distilled water in a 1-liter beaker. Add 57 ml conc. acetic acid, 58 g. sodium chloride and 12 g. sodium citrate. Stir to dissolve.

b Place the beaker in water bath (for cooling), insert a calibrated pH electrode and a reference electrode into the solution and slowly add approximately 6N sodium hydroxide until the pH is between 5.0 and 5.5. Put into a 1-liter volumetric flask and add distilled water to the mark. Mix well.

2 Fluoride stock solution

a Dissolve 0.2210 g. sodium fluoride in 1 liter of distilled water (1 ml = 0.1 mg F).

3 Standard fluoride solution

a Dilute 20 ml of the above stock solution to 1 liter (1 ml = 0.002 mg F).

B Procedure

1 Prepare a series of standards by pipetting the indicated amounts of standard fluoride solution into labeled 150-ml beakers, adding the indicated amounts of distilled water (by pipet), and then adding 50 ml of TISAB to each.

Ml Standard Soln.	ml Dist. Water	mg F	ppm F
5	45	0.01	0.2
10	40	0.02	0.4
15	35	0.03	0.6
20	30	0.04	0.8
25	25	0.05	1.0
50	0	0.10	2.0

2 In 150-ml beakers place by pipet 50 ml samples. Add 50 ml of TISAB to each. Bring standards and samples to the same temperature (plus or minus 2°C).

3 Immerse the electrodes and measure the developed potential while stirring the test solutions with a magnetic stirrer. Allow the electrodes to remain in the solution for 3 minutes before taking a final mv reading. Rinse electrodes with distilled water and blot dry between each reading. Record mv reading for each standard.

4 Read samples similarly. Confirm the electrode calibration by checking the reading of the 1.0 ppm standard between samples.

5 Plot the potential measurement CF Standards in mv along the arithmetic horizontal axis of 2-cycle semi-logarithmic graph paper. Plot ppm on the vertical logarithmic axis, starting with 0.1 ppm at the bottom.

6 Read the fluoride concentration of the unknown samples from the standard curve prepared from the readings obtained on the standards.

II ELECTRODE METHOD USING PORTABLE METER

A Reagents

1 TISAB

a Prepare as for regular Electrode Method, or

b Use commercially prepared TISAB or Fluor-Ade buffer

2 Standard fluoride solution

a Dilute fluoride stock solution 1:10 with distilled water to make 10 ppm F standard (1 ml = 0.01 mg F) and dilute fluoride stock solution 1:100 with distilled water to make 1 ppm F standard, or

b Use commercially prepared standards.

B Procedure

1 Prepare two standards:

a In a beaker labeled "1.0 ppm" add by pipet 10 ml of the 1.0 ppm fluoride standard solution or about 20 ml of commercial 1.0 ppm standard.

b In a beaker labeled "10 ppm" add by pipet 10 ml of the 10.0 ppm fluoride standard solution (1 ml = 0.01 mg F) or about 20 ml of the commercial 2.0 ppm standard.

2 Add 10 ml (by pipet) of TISAB to each of the standards. Commercial standards already have TISAB added so require no further treatment.

3 Pipet 10 ml of samples into labeled beakers. Add 10 ml of TISAB to each.

4 Immerse the electrodes in the 1.0 ppm standard. Set the selector of a Model 401 meter on "F" and swirl the beaker gently for 3 minutes. On the Model 409 meter the selector should be set at "0.5 - 2".

5 Adjust the meter so that the pointer reads 1.0 ppm. Use the calibration knob on a Model 401 or the "0.5 - 2" knob on a Model 409.

6 Turn off the meter, lift the electrodes, rinse them in distilled water and pat dry with a tissue.

7 Immerse the electrodes in the 10 ppm or 2 ppm standard, set the selector of a Model 401 meter on "F" or that of a Model 409 on "0.1 - 10" and swirl the beaker gently for 3 minutes. Adjust the meter until the pointer indicates the proper concentration, using the Temperature Compensator on a Model 401 or the "0.1 - 10" knob on a Model 409. Turn off the meter, rinse and dry the electrodes after each use.

8 Immerse the electrodes in a sample, set the meter selector to "F" or "0.5 - 2", swirl the beaker gently for 3 minutes and read the fluoride concentration directly from the meter scale.

USE OF INSTRUMENTS

I THE CHOICE OF INSTRUMENT FOR THE PHOTOMETRIC FLUORIDE METHOD IS GOVERNED BY NEED, COST AND VERSATILITY

A A Spectrophotometer is More Sensitive and More Versatile than a Filter Photometer, but is Also More Expensive.

B A Filter Photometer is Lower in Cost, but may be Less Sensitive.

II A spectrophotometer of the diffraction-grating type will be used in this course for the SPADNS procedure. It is operated as follows:

A Set the wave-length at 570. Adjust the dark current to zero after the instrument has warmed up. (Figure 1)

B Place a cuvette containing a 0 ppm standard, to which reagent has been added, in the instrument. Close the cell cover and adjust the slit until an absorbance reading of 0.500 is obtained. (Inserting the cuvette in the cell compartment automatically opens the shutter).

C Replace the 0 ppm standard with other standards or samples and record absorbance readings. Occasionally recheck the dark current and 0 ppm standard and adjust if necessary. Always set the dark current at zero before making subsequent readings.

III PERMANENT COLOR STANDARDS COMPARATORS MAY BE USED FOR FLUORIDE ANALYSIS PROVIDED:

A Standards are Checked Against Standard Samples Prepared by the Analyst at Least Once for Each Batch of Reagent.

B Reagents are Prepared from Concentrates Furnished by the Manufacturer.

C Manufacturer's Instructions, Particularly Those Regarding Time and Temperature, are Closely Followed.

D Light Intensity for Both Sample Tubes is Balanced.

E Glassware is Matched.

IV THE CHOICE OF INSTRUMENT FOR THE ELECTRODE METHOD IS GOVERNED BY NEED AND COST

A A Digital Meter Capable of Being Read to the Nearest 0.1 mv Gives the Best Accuracy.

B An Expanded-Scale pH Meter is More Difficult to Read, but is Usually Less Expensive and may be Already on Hand.

C Specific-Ion Meters (Portable) are More Convenient, but Less Accurate.

V THE OPERATING PROCEDURE VARIES WITH THE TYPE OF pH METER.

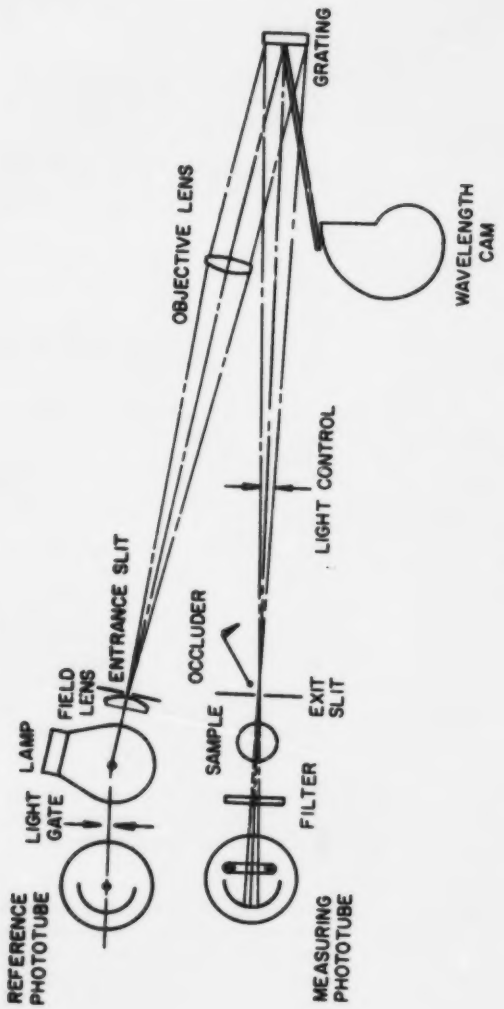
A For those instruments with zero at center-scale, adjust the calibration control so that the 1.0 ppm F standard reads at the center zero (100 mv) when the meter is in the expanded scale position.

B Most digital and other pH meters normally require no adjustment. If the instrument has one, the calibration control can be used to compensate for electrode drift by adjusting the instrument to give the same reading for a 1.0 ppm F standard as it did when the calibration curve was prepared. This eliminates the need for preparation of a whole series of standards each time the instrument is used.

C In the case of a specific-ion meter, follow the instructions of the manufacturer for calibrating the instrument.

VI Several devices have been built which automatically determine and record fluoride in water on a continuous or semi-continuous basis. Some of the principles of operation of these devices are as follows:

A Volumes of sample and reagent are metered out, mixed and passed through a colorimeter. The scale reading of the colorimeter is then transposed to a chart whose scale is calibrated in units of fluoride concentration.



OPTICAL SYSTEM OF SPECTRONIC 20 SPECTROPHOTOMETER FIG. 1

B Samples of water are continuously double-distilled and the resulting solution passed through a conductivity cell. Conductivity units are then interpreted as fluoride concentration.

C Samples of water, to which buffer and other reagents have been added, are continuously fed through an electrolytic cell containing a rotating aluminum electrode and a stationary electrode. The current generated is interpreted as fluoride concentration.

D Water flows continuously past electrodes similar to those used in the electrode method and the voltage potential is interpreted as fluoride ion activity.

CONTROL OF INTERFERING IONS

I The principal source of error in fluoride analysis is the presence of interfering ions. This is particularly true in the colorimetric methods, as can be seen from Table I which lists some ions commonly found in water and their affect on the Standard Methods fluoride analyses.

A In colorimetric analysis, one of the mechanisms by which these ions cause error is the changing of the reaction rate. Since the determination is based on color development, variations in reaction rate cause variations in fluoride reading.

B Some ions complex with either fluoride, in all methods, or with zirconium, in the colorimetric methods. When fluoride is complexed, low results are obtained, and when zirconium is complexed, the intensity of color is altered.

C Chlorine bleaches out the colors of dyes, and must always be removed before the sample can be analyzed colorimetrically.

II Whenever the quantity of interfering ions in the water is sufficient to cause an error of 0.1 ppm fluoride or more, or whenever the analysis is unknown, these interferences must be removed or their effects diminished by one of the following methods:

A If the interferences are known to be caused by chemicals added during treatment in the water plant, they may sometimes be avoided by appropriate selection of a sampling point within the plant.

B In some cases the water sample can be diluted to bring the level of an interfering ion below the critical point. This procedure is applicable only when the fluoride level is sufficiently high to permit accurate analysis on the diluted sample.

C When the identity of the interfering ion is known, it may be possible to select an analytical method which has adequate tolerance for that ion.

TABLE I. INTERFERENCES

Concentration of Substance, in Mg/L, Required to Cause an Error of Plus or Minus 0.1 Mg/L at 1.0 Mg/L F.

	Scott-Sanchis	SPADNS	Electrode
Alkalinity	400 (-)	5,000 (-)	7,000 (+)
Aluminum	0.25 (-)	0.1 (-)*	2.0 (-)
Chloride	2,000 (-)	7,000 (+)	20,000 (-)
Iron	2 (+)	10 (-)	200 (-)
Hexametaphosphate	1.0 (+)	1.0 (+)	>50,000
Phosphate	5 (+)	16 (+)	>50,000
Sulfate	300 (+)	200 (+)	50,000 (-)
Chlorine	Must Be Completely Removed With Arsenite		> 5,000
Color & Turbidity	Must Be Removed or Compensated For.		-----

*Above Figure is for Immediate Reading. Allowed to Stand Two Hours Tolerance is 3.0 Mg/L. Four Hour Tolerance is 30 Mg/L.

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D When the composition of the unfluoridated water is known and constant, equivalent quantities of interfering ions can be added to the fluoride standards, thereby neutralizing the effect of those ions.

E In all other cases the water sample must be distilled. As can be seen from Table I, distillation will seldom be necessary when the electrode method is used.

III The principle of the distillation process is the conversion of fluoride to the volatile acid, H_2SiF_6, in the presence of sulfuric acid and silica (glass beads). The fluosilicic acid distills over, leaving most of the interfering ions behind.

A The apparatus used is illustrated in Figure 1. It consists of a distillation flask, connecting tube and condenser. For convenience, apparatus with ground-glass joints is used, but a simpler arrangement using rubber stoppers is satisfactory (Figure 2).

B The critical features of the apparatus are the diameter of the connecting tube, the immersion of the thermometer, and fit of stoppers and/or ground-glass joints.

1 The diameter of the connecting tube must be large enough to preclude the carryover of bubbles.

2 The thermometer must be positioned low enough so that it will always be immersed.

3 Stoppers and joints must be tight enough to prevent the loss of fluoride-containing vapor.

C The Distillation Procedure is Carried Out as Follows:

1 Prepare the still by placing 400 ml distilled water, some glass beads and then 200 ml concentrated acid in the flask. Add the acid slowly and stir thoroughly. After all the acid has been added, stir again until the mixture is homogeneous.

2 Connect the apparatus as shown in the drawing, start water through the condenser and begin heating slowly. If bumping occurs, the acid and water have not been mixed sufficiently. When boiling starts, heating may be increased.

3 Continue heating until the temperature reaches 180°C. Discard this distillate, since it contains traces of fluoride from the acid and glassware. This preliminary procedure also serves to adjust the acid-water ratio for subsequent distillations.

4 Allow the flask to cool until the temperature drops to 120° C or lower. Measure out a 300-ml sample and add it to the flask. Mix thoroughly.

5 Distill as before until the temperature reaches 180°C. Retain the distillate (there should be 300 ml) for colorimetric determinations.

D The distillation process must be carried out very carefully, since there are several possible sources of difficulty.

1 The flame under the distillation flask must never touch the sides of the flask above the liquid level. Superheating of the vapor results in high sulfate carryover which causes a sulfate interference.

2 All stopper and joints must fit tightly to prevent loss of fluoride.

3 Flask contents must be thoroughly mixed to prevent bumping.

4 Distillation must be stopped when the temperature reaches 180°C. Higher temperatures result in excessive sulfate carryover.

5 Silver sulfate, at the ratio of 5 mg/mg of Cl, should be added when high-chloride samples are distilled. The presence of silver inhibits the volatilization of HCl which, in sufficient quantity, could interfere with the fluoride determination.

6 When high-fluoride samples are distilled, repeat the distillation using 300 ml of distilled water. Analysis of the distillate will indicate how complete the fluoride recovery was. If substantial amounts of fluoride appear in the second distillate, add the quantity to that obtained initially and flush again. Quantities of less than 0.1 ppm F (0.03 mg) may be disregarded.

7 Because of the simplicity of apparatus and procedure, the distillation procedure can be readily automated. Modifications include magnetic stirring and a thermostat which turns off a quartz heating mantle when the correct temperature has been reached.

Fig. 1 DISTILLATION APPARATUS

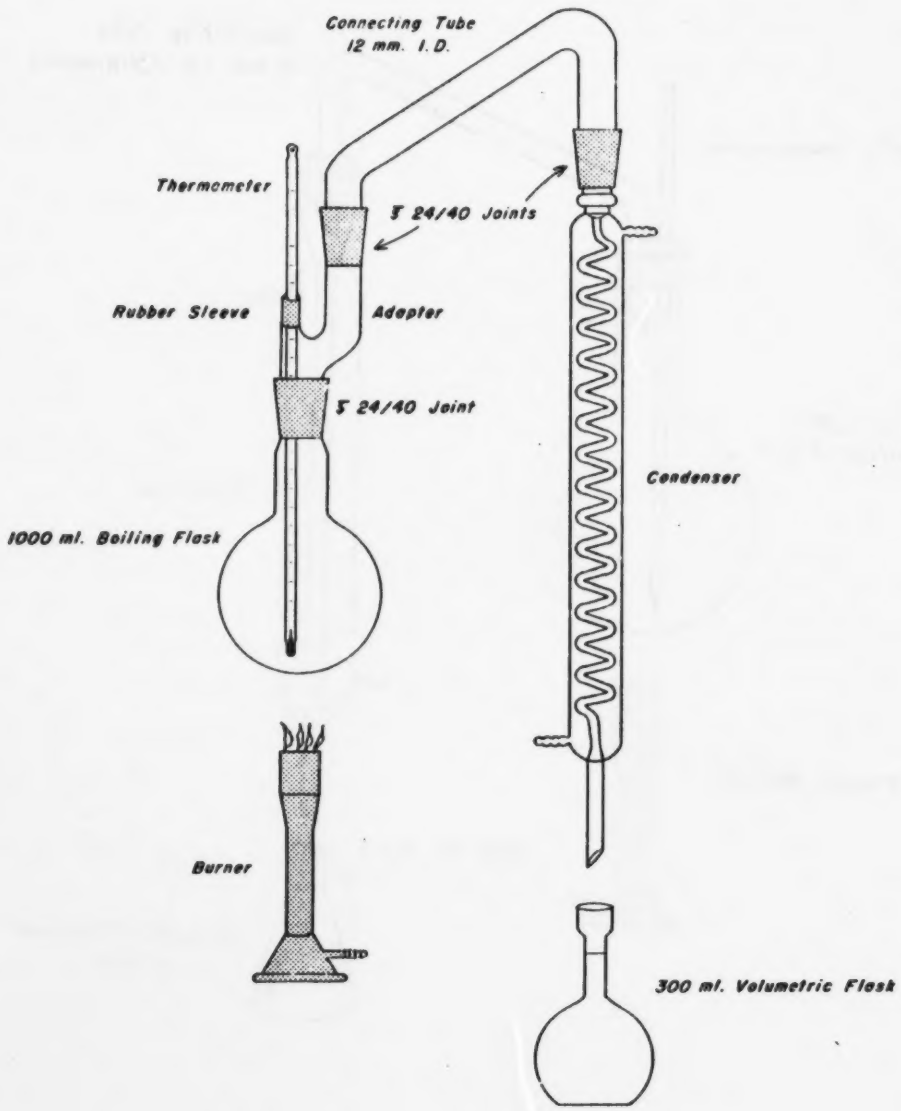
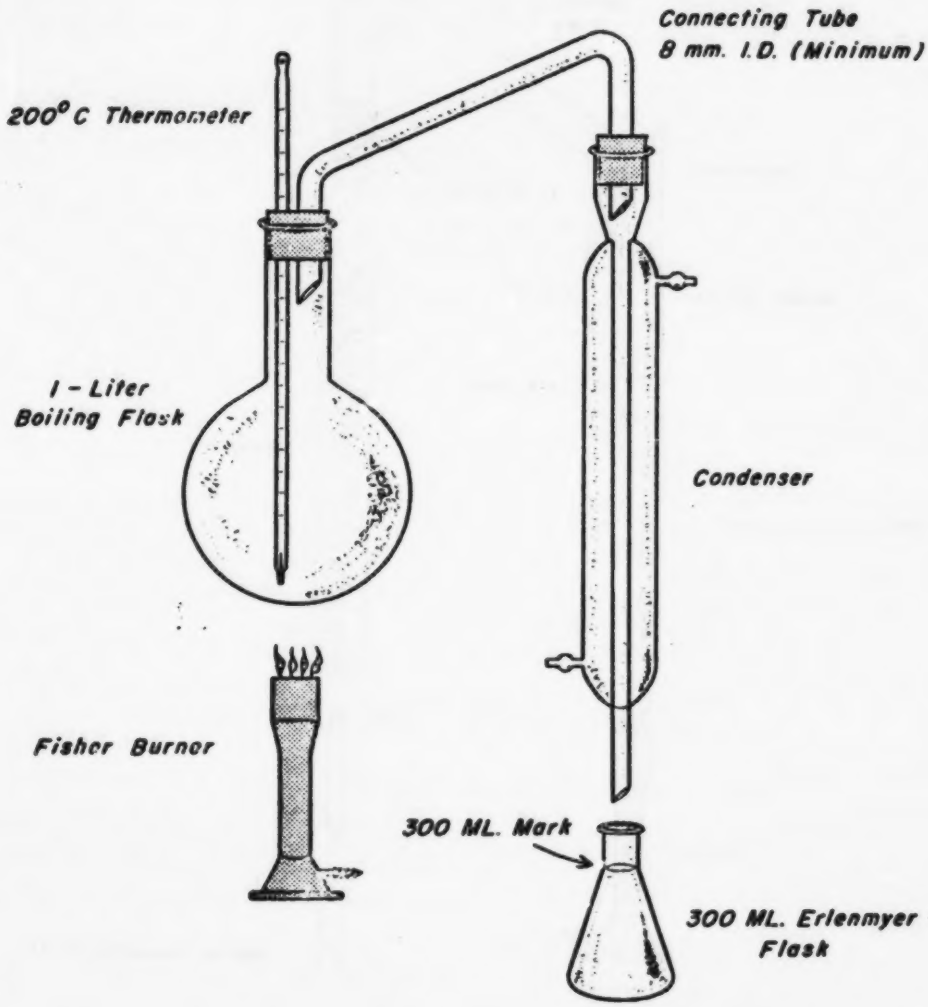


Fig. 2 SIMPLIFIED DISTILLATION APPARATUS



FLUORIDE LABORATORY

Session 1

Determination of Fluoride in Water

Samples:

I and II, containing different concentrations of fluoride, with no interfering substances.

Procedure:

1 Determine fluoride concentration of samples I and II using both colorimetric methods.

2 Record results on Data Sheet.

Session 2

Removal of Interferences by Distillation

Samples:

III and IV, containing interfering substances.

Procedure:

1 Distill a single 300-ml aliquot of each sample.

2 Hold distillates for Session 3.

Session 3

A Determination of Fluoride in the Presence of Interferences

Samples:

III and IV, from Session 2.

Procedure:

1 Using Scott-Sanchis method, determine fluoride concentration of a 100-ml aliquot of each of the distillates from Session 2. Also determine fluoride concentration of a 100-ml aliquot of each of the undistilled samples from Session 2.

2 Using SPADNS method, determine fluoride concentration of a 50-ml aliquot of each of the distillates from Session 2. Also determine fluoride concentration of a 50-ml aliquot of each of the undistilled samples from Session 2.

3 Record results on data sheet.

B Fluoride Analytical Procedures-Electrode

Samples:

III and IV containing interfering substances.

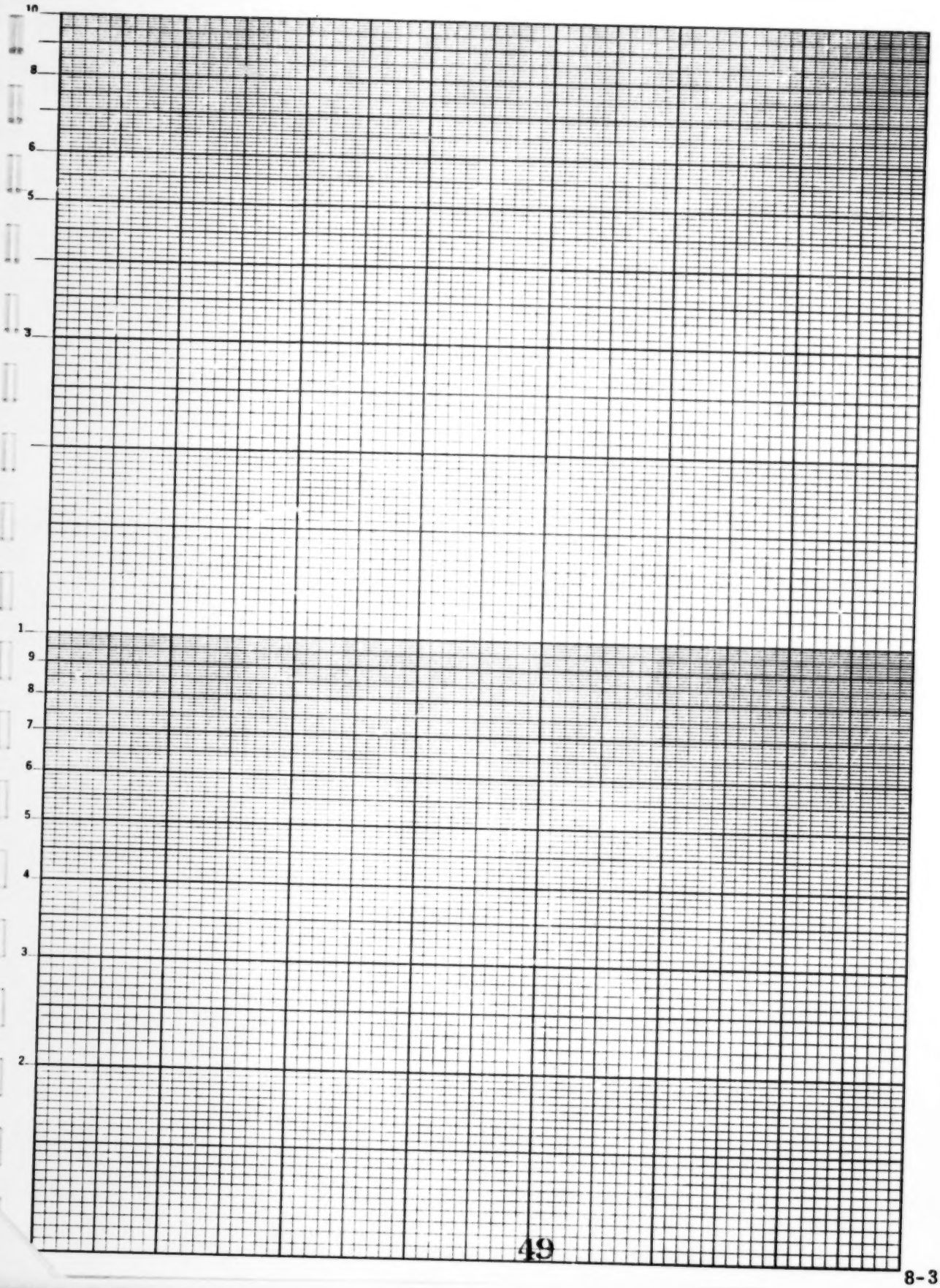
Procedure:

1 Determine the fluoride concentration of samples III and IV using the electrode method.

2 Record results on data sheet.

DATA SHEET

Sample No.	Method	Sample Volume (ml)	ppm Fluoride
I	Scott-Sanchis	100	_____
	SPADNS	50	_____
II	Scott-Sanchis	100	_____
	SPADNS	50	_____
III (undistilled)	Scott-Sanchis	100	_____
	SPADNS	50	_____
	Electrode	50	_____
III (distilled)	Scott-Sanchis	100	_____
	SPADNS	50	_____
IV (undistilled)	Scott-Sanchis	100	_____
	SPADNS	50	_____
	Electrode	50	_____
IV (distilled)	Scott-Sanchis	100	_____
	SPADNS	50	_____



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